

PREFERENCE FOR TOP- VS. SIDE-BINDING IN FLUORINATED ETHYLENE...CO₂ COMPLEXES

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The weakly bound complexes between 1-fluoroethylene (FE), 1,1-difluoroethylene (DFE), and 1,1,2-trifluoroethylene (TFE) and carbon dioxide have been investigated using reduced bandwidth chirped-pulse (CP) and resonant-cavity Fourier-transform microwave (FTMW) spectroscopy. In FE...CO₂, two distinct planar isomers are observed, corresponding to the CO₂ interacting with the CHF end of the FE (side-binding) or roughly parallel to the C=C bond (top-binding). Both structures contain a C-H...O contact between one FE hydrogen atom and CO₂. In DFE...CO₂, only a top-binding configuration is possible, consistent with the observed structure. Finally, although both top- and side-binding orientations are possible for TFE...CO₂, only the side-binding conformation has been observed. The C-H...O distances in the four species vary from 2.58 Å to 2.73 Å, while the observed F...C distances are much more consistent, varying by only about 0.05 Å across the series. Ab initio calculations at the MP2/6-311++G(2d,2p) level have provided exceptionally accurate estimates of the rotational constants of these CO₂ complexes, although the energy ordering is, in several cases, inconsistent with the observed geometries.